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Thermodynamic properties of CdNa alloys

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Abstract : The alloying behaviour of CdNa alloys is discussed on the basis of a simple theory based on the complex formation model. Though Cd and Na are simple metals but CdNa alloys exhibit anomalous behaviour. The excess free energy of mixing is negative in the region $0.6 \leq C_{Na} > 0.1$ and thereafter becomes positive. The concentration-concentration fluctuations in the long wavelength limit $Scc(0)$ is larger than the ideal values $Scc(0,id)$ up to $C_{cd} = 0.55$ and is less than ideal values for $C_{cd} > 0.55$. The concentration-dependent nature of asymmetry of the thermodynamic properties of mixing have been explained in this paper. The study reveals that Cd_2Na complex exists in the liquid phase close to melting temperature.

Keywords : Cd Na alloys, thermodynamic properties, concentration-concentration fluctuations, volume of mixing, Free energy of mixing

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The thermodynamic properties of many binary liquid alloys [1] deviate from their ideal values. The concentration-dependent properties of CdNa liquid alloys [2,3] are interesting in many ways. The excess free energy of mixing (G_M) and volume of mixing (ΔV_M) are quite asymmetrical around the equi-atomic composition. Recently, a considerable effort [4] is made to understand asymmetry by considering the existence of chemical complexes [$\mu A + \upsilon B \rightleftharpoons A\mu + B\upsilon$, A and B are the constituent species and μ and υ are small integers]. Many workers have explained the anomalous behaviour of the alloys [5–10, 13–17] in compositional plane.

In the present work, a simple theory based on the complex formation model [4] has been considered to explain the concentration-dependent long wavelength range concentration-concentration fluctuation Scc(o), free energy of mixing (G_M) and volume of mixing (ΔV_M) have been investigated.

Let n_1, n_2 and n_3 are gm moles of A atoms, B atoms and $A\mu B\upsilon$ in the mixture, then choosing Avogadro's number N=1 and following [5, 7, 10–12], we have

$$n_1 = C - \mu n_3, \quad n_2 = 1 - C - \mu n_3,$$
$$n = n_1 + n_2 + n_3 = 1 - (\mu + \upsilon - 1)n_3. \qquad (1)$$

Here, C and $(1-C)$ are concentrations of the atoms A and B respectively.

The free energy of mixing G_M of binary alloy may be written as [5]

$$G_M = -n_3 g + G', \qquad (2)$$

where g is the formation energy of the complex and G' is the energy of mixing of the ternary mixture consisting of A atoms, B atoms and the complexes $A\mu$ $B\upsilon$.

The equilibrium values of n_3 has been determined *via* the condition :

$$\left(\frac{\partial G_M}{\partial n_3}\right)_{T,P,C} = 0 \qquad (3)$$

The Flory's expression for the free energy of mixing, G' of the ternary mixture can be written as

$$G' = RT\left[n_1 l_n n_1 + n_2 l_n n_2 + n_3 l_n (\mu + \nu) n_3\right]$$
$$+ \sum\sum_{i<j} n_i n_j v_{ij}, \qquad (4)$$

where v_{ij} (= 0 if $i = j$) are the interchange energies. Using eqs. (4) and (2), we have

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$$G_m = -n_3 g + RT\left[n_1 l_n n_1 + n_2 l_n n_2 + n_3 l_n (\mu+\nu) n_3\right] + \sum\sum_{i<j} n_i n_j v_{ij}. \quad (5)$$

With eqs. (3) and (5), the equilibrium value of n_3 is obtained by the equation :

$$\frac{n_1^{\mu} n_2^{\nu}}{} = (\mu+\nu) K e^{(\mu+\nu-1)} e^{z}, \quad (6)$$

where $K = e^{-g/RT}$, (7)

$$Z = 1/RT[(n_1 - \mu n_3)v_{13} + (n_2 - \mu n_3)v_{23} - (\mu n_2 - v_{n1})v_{12}]. \quad (8)$$

The concentration-concentration fluctuations in the long wavelength limit can be expressed as

$$Scc(o) = RT/\frac{\partial^2 G_M}{\partial^2 C^2} \quad (9)$$

With eqs. (5), (6) and (1), we have $Scc(o)$ from eq. (9) as

$$Scc(o) = 1/\begin{vmatrix} n_1'^2 & n_2'^2 & n_3'^2 \\ n_1 & n_2 & n_3 \end{vmatrix} + \frac{2}{RT}[v_{12}(n_1'n_2') + v_{13}(n_1'n_3') + v_{23}(n_2'n_3')], \quad (10)$$

where a prime represents differentiation with respect to C. n_3' can be obtained from eq. (6) using eq. (1) and keeping in the mind that

$$ni/n = (n_i'n - n'n_i)/n^2. \quad (11)$$

Eq. (3) and (4) can also be used to obtain an expression for activity a_A of the atom A as

$$RT \ln a_A = G_M + (1-C)\frac{\partial G_M}{\partial C} \quad (12)$$

which yields,

$$\ln a_A = \ln(n_1/n) - 1 + \ln n - n + 1/RT\left[n_3 v_{13} + n_2 v_{12}\right] - 1/RT + \sum\sum_{i<j} n_i n_j v_{ij}. \quad (13)$$

Experimental values of $Scc(o)$ is obtained from the observed value of activities [1] using the relation

$$Scc(o) = (1-C)\frac{a_A}{\partial a_A/\partial_C} = \frac{Ca_B}{\partial a_B/\partial(1-C)}, \quad (14)$$

where a_A and a_B are the activities of atom A and atom B, respectively. Recently, Harada *et al* [3] have measured emf in liquid Na-Cd alloys over a wide range of concentrations and hence obtained $Scc(o)$.

Hoshino *et al* [2] observed the volume of mixing of CdNa liquid alloys and found a large volume contraction. We have therefore used eq. (2) to obtain the concentration dependence of ΔV_M, *i.e.*

$$\Delta V_M = V - CV_A^{(O)} - (1-C)V_B^{(O)}\left(\frac{\partial G_M}{\partial P}\right)_{C,n_i} \quad (15)$$

From eq. (3), we get

$$\Delta V_M = -n_3\left(\frac{\partial g}{\partial P}\right) + \sum\sum_{i<j} n_i n_j \left(\frac{\partial v_{ij}}{\partial P}\right). \quad (16)$$

Using eq. (16), ΔV_M are computed with the previous knowledge of n_1, n_2 and n_3, the pressure derivatives of interaction energies are treated as parameters. Variation of ΔV_M with concentration are plotted in Figure 1.

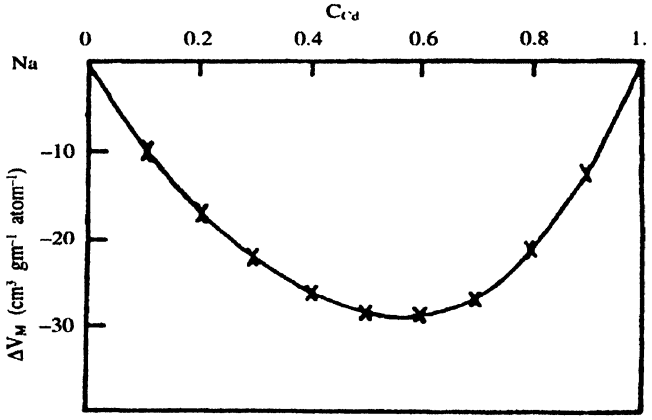

Figure 1. Variation of volume of mixing ΔVm of CdNa alloys at 673°K (——) theory and (x x x x) expt. [2].

The computed values of free energy of mixing (G_m/RT), activity (a_{cd}) and the concentration fluctuations $Scc(o)$ are tabulated in the Table 1 along with the experimental

Table 1. Computed and experimental values of $G_{M/RT}$, activity and $Scc(o,id)$ of CdNa alloys.

C_{cd}	$G_{M/RT}$		Activity		$Scc(o)$		$Scc^{id}_{(O)}$
	Th.	Expt.	Th.	Expt.	Th.	Expt.	
0.1	–0.2460	–0.2701	0.138	0.138	0.227	0.175	0.09
0.2	–0.4222	–0.4376	0.177	0.193	0.499	0.370	0.16
0.3	–0.5770	–0.5775	0.202	0.226	0.592	0.585	0.21
0.4	–0.7142	–0.6987	0.228	0.253	0.465	0.515	0.24
0.5	–0.8293	–0.8004	0.264	0.290	0.294	0.910	0.25
0.6	–0.9092	–0.8678	0.323	0.353	0.164	0.172	0.24
0.67	–0.9302	–	0.393	–	0.103	–	0.221
0.7	–0.9258	–0.8768	0.435	0.460	0.085	0.102	0.21
0.8	–0.8228	–0.7870	0.638	0.623	0.054	0.066	0.16
0.9	–0.5389	–0.5296	0.858	0.848	0.046	0.035	0.09

values [1]. The experimental values of $Scc(o)$ have been directly observed from measured activity data using the relation (14). The energy parameters which have been used in the calculations are as follows :

$K = 0.19$, $v_{12/RT} = 2.1$, $v_{13/RT} = 0.00$, $v_{23/RT} = 2.25$. Here, $K = e^{-g/RT}$ and g is the formation energy of the complex. Smaller values of $g/_{RT}$ indicates that the tendency of compound formation in CdNa system is not so strong as in other strong interacting system such as MgBi, HgK *etc.* for which $g/_{RT}$ is large. If g and $v_0/_{RT}$ are made concentration-dependent, then the very structure of the complex formation model weakens.

The computed values of $G_{M/RT}$ are in good agreement with the experimental values. The computed values of activity also agree well with the observed values. The minimum values of $G_{M/RT}$ *i.e* -0.9302 has been obtained at $C_{cd} = 0.67$ which is the stoichiometric composition. From Figure 1, we observe that the minimum in ΔV_M occurs around $C_{cd} = 0.6$. We observe that though CdNa alloy is a weak interacting system ($G_{M/RT} = -0.33$), the molar volume undergoes a large volume contraction, similar to strong interacting alloys *e.g* HgNa [11] and LiPb [12].

The two sets of data for $Scc(o)$, our computed values and the values obtained from measured emf values by Harada *et al* [3], are in good agreement with one another (Figure 2) and are quite asymmetric as a function of concentration. Because of $Scc(o)$ being a response function, it requires to be positive. A strong response to a concentration separation stimulus shows that system is near phase separation, while a weak one indicates a nearness to complex formation. In the limit,

$Scc(o) = \infty$ (Phase separation)

$= o$ (Compound formation).

Apart from limiting behaviour given above, the deviation of $Scc(o)$ from ideal values $Scc(o,id)$ is sufficient to inform the nature of atomic order present in the alloy. They exhibit only a weak deepening around the concentration Cd_2Na. It may be mentioned that sometimes (as in NaCs), the size effect [18, 19] is also responsible for producing asymmetry in the properties of mixing and $Scc(o)$. In CdNa alloys, the observed asymmetry can not be explained just by considering the size effect.

The values of $Scc(o)$ reveals that CdNa liquid alloy deviates greatly from the ideal solution values. The perusal of $G_{M/RT}$, activity, ΔV_M and $Scc(o)$ data reveal that Cd_2Na complexes exist in the melt but of weak interaction.

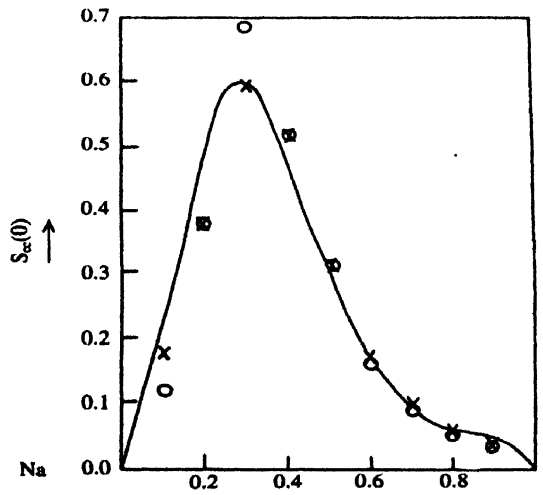

Figure 2. Variation of $Scc(o)$ of CdNa alloys at 673°K (– –), theory; (x x x x) expt; (o o o o) Harada *et al* [3].

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